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Review

Near-zero-waste processing of low-grade, complex primary ores and secondary raw materials in Europe: technology development trends



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ABSTRACT

With an increasing number of low-grade primary ores starting to be cost-effectively mined, we are at the verge of mining a myriad of low-grade primary and secondary mineral materials. At the same time, mining practices and mineral waste recycling are both evolving towards sustainable near-zero-waste processing of low-grade resources within a circular economy that requires a shift in business models, policies and improvements in process technologies. This review discusses the evolution towards low-grade primary ore and secondary raw material mining that will allow for sufficient supply of critical raw materials as well as base metals. Seven low-grade ores, including primary (Greek and Polish laterites) and secondary (fayalitic slags, jarosite and goethite sludges, zinc-rich waste treatment sludge and chromium-rich neutralisation sludge) raw materials are discussed as typical examples for Europe. In order to treat diverse and complex low-grade ores efficiently, the use of a new metallurgical systems toolbox is proposed, which is populated with existing and innovative unit operations: (i) mineral processing, (ii) metal extraction, (iii) metal recovery and (iv) matrix valorisation. Several promising novel techniques are under development for these four unit-operations. From an economical and environmental point of view, such processes must be fitted into new (circular) business models, whereby impacts and costs are divided over the entire value chain. Currently, low-grade secondary raw material processing is only economic and environmentally beneficial when the mineral residues can be valorised and landfill costs are avoided and/or incentives for waste processing can be taken into account.

1. Introduction

Economically important metal and mineral raw materials are deemed “critical” when their risk of supply shortage is high (European Commission, 2017). Such definition implies that the criticality of a raw material is determined by geopolitics (e.g. distance to

material source and accessibility through trading agreements) and that it can change over time (e.g. due to changes in market demand). The geopolitical dimension can be illustrated by differences in the lists of raw materials assigned to be critical for different regions in the World (see Supplementary Information), while the change over time is illustrated by the fact that the *critical raw materials* (CRMs) lists drawn up

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by the European Commission in 2011, 2014 and 2017 contained 14, 20 and 27 critical raw materials, respectively (European Commission, 2017; Hatayama and Tahara, 2015; Schulz et al., 2017). Critical raw materials are important for the competitiveness of the manufacturing sector and for innovations in high-tech sectors (European Innovation Partnership on Raw Materials, 2018; Reuter, 2013).

Furthermore, base metals, e.g. aluminium, copper, zinc and nickel, are irreplaceable for many products in the automotive, aerospace, mechanical engineering, and construction sectors. Their unique thermal, mechanical, electrical, and isolating characteristics coupled with good recyclability make them indispensable. In practice, the European Union (EU) is one of the biggest consumers of non-ferrous metals worldwide and its dependence on imported raw materials to produce metals and metal products is growing rapidly. In several cases, the differences in material imports and exports of the EU (Eurostat data from 2017) are significant (Supplementary Information).

The easy-to-access EU CRM and base metal deposits have been exhausted, leading to a situation where the remaining ores are more complex and of lower grade. Apart from having low-grade primary ore deposits (Minerals4EU, 2014), Europe also possesses large amounts of metals which are locked up in industrial process residues, such as tailings, metallurgical sludges, slags, dusts and ashes (Binnemans et al., 2015; Borra et al., 2016; Edraki et al., 2014; Lèbre et al., 2017). Therefore, these materials could be named *secondary resources* or *secondary raw materials*, as they can be identified as *materials and products which can be used as raw materials by simple re-use or via recycling and recovery* (European Commission, 2020). Such secondary raw materials do not only contain unharvested critical raw materials, but also base metals (e.g. Zn, Pb, Cu) at grades that are becoming competitive with the decreasing grades of primary ores. However, the traditional pyrometallurgical and hydrometallurgical processes that were designed for high-grade ores are often not efficient for recovery of metals from low-grade ores and industrial process residues so that new tailored processes must be designed (Konnitsas, 2019).

The *zero-waste concept* (Binnemans et al., 2015; Curran and Williams, 2012; Zaman, 2015) envisions a closed-loop use of all available resources and thus embraces the full recovery and valorisation of both metals and the residual matrix material (*i.e.* the metal depleted mineral residue that directly derives from the primary ore and secondary raw material after the metal extraction process). Therefore, implementation of this concept is seen as one of the pre-requisites towards the principles of a circular economy (Ghisellini et al., 2016). Kirchherr et al., 2017 defined circular economy based on an extensive review as following: “A circular economy describes an economic system that is based on business models which replace the ‘end-of-life’ concept with reducing, alternatively reusing, recycling and recovering materials in production/distribution and consumption processes, thus operating at the micro-level (products, companies, consumers), meso-level (eco-industrial parks) and macro-level (city, region, nation and beyond), with the aim to accomplish sustainable development, which implies creating environmental quality, economic prosperity and social equity, to the benefit of current and future generations”. Because production of metals without generation of any waste is (virtually) impossible, one must aim for near-zero-waste processes. To reduce the current waste production near to zero, industrial symbioses and development of new (recycling) technologies need to be stimulated. Although still at its infancy, the application of the zero-waste principle to metal-containing mineral waste materials and low-grade primary ores is gaining interest in the scientific literature. For instance, Binnemans et al., 2015 emphasised the need for “new metallurgical systems” to allow for the zero-waste valorisation of low-grade rare earth element containing mineral waste materials, such as phosphogypsum and bauxite residue. Kim et al., 2016 have proposed a process to fully recycle stainless steel slag by a combination of chromium extraction and subsequent carbonation of the cleaned mineral residue to new building applications. A search of the existing literature

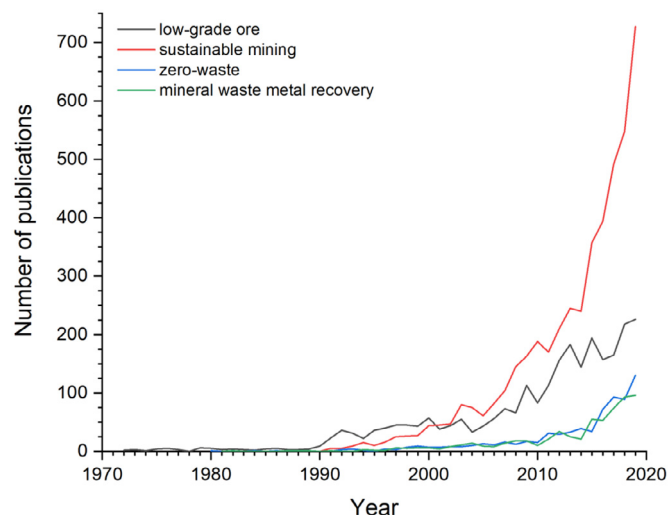


Figure 1. Number of scientific publications, according to Web of Science*, that correspond to the search terms “low-grade ore”, “sustainable mining”, “zero-waste” and “mineral waste metal recovery” on 20/03/2020 (*a Clarivate Analytics product)

via search terms related to mining, such as “sustainable mining” and “low-grade ore”, and to (mineral) waste processing, such as “zero-waste” and “mineral waste metal recovery”, indicates that the two mining-related topics started to enjoy increasing attention from the early 1990s onward, whereas the waste-related topics gained importance since about one decade ago (Figure 1).

This review gives an overview of the economic, social, environmental and technology developments that can enable treatment of currently untapped primary and secondary low-grade metal resources. Furthermore, it aims to highlight the evolution towards near-zero-waste processing of low-grade ore and metal-containing industrial process residues in a circular economy, with a particular focus on Europe.

2. Evolution of metal production and waste recycling towards a zero-waste approach

Both the metal production and waste recycling industries have been facing substantial changes over time. Whereas the changes in the metallurgical industry occurred over a period of several millennia (Agricola, 1950), the evolution of current day recycling took place in the much more confined period of the recent decades.

Pyrometallurgy and hydrometallurgy have approximately 6000 and 500 years of history, respectively (Canterford, 1985). The first metallurgical extraction processes were pyrometallurgical and extracted copper, later they produced bronze and eventually they led to the production of iron and steel. Hydrometallurgy came into play more recently, when iron scrap was used in the early 16th century to recover copper from acid mine drainage by cementation (Habashi, 2005), for instance at the Rammelsberg mine in Goslar, Germany (Brockner, 2000). Hydrometallurgy allowed for the extraction of metals present in complex matrices and at a lower concentration; it can be also used for the treatment of ores and concentrates and the recovery of metals in smaller processing plants compared to pyrometallurgy (Canterford, 1985). The mineralogy of the ore largely affects the selection of the most appropriate processing route for low-grade ores, when energy consumption for processing and greenhouse gas emissions are taken into account (Norgate and Jahanshahi, 2010). Often pyro- and hydrometallurgical processes are combined in one process flow sheet (Canterford, 1985).

Since the early 1980s, *responsible mining* became an important criterion in mining and metal extraction. Although this term can be interpreted and applied in different ways, ranging from economic to

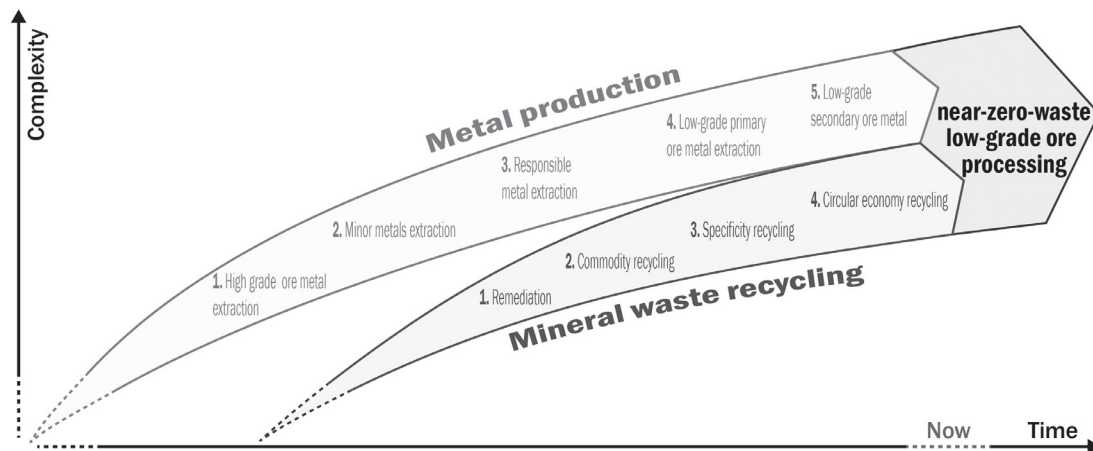


Figure 2. Scheme representing the natural approach and final cross-over of research challenges regarding metal recovery within the mineral waste treatment and extractive metallurgy of primary ore.

environmental to social aspects (Broad, 2014), its general effect on the extraction processes was more strict legislation with regard to residue containment and treatment and the need for the development of less polluting technologies. Furthermore, an optimisation of the mining and metal extraction industrial processes according to sustainability principles is required, although according to Goodland (2012) mining in itself cannot be defined sustainable due to its resource-depleting nature.

Regardless of responsible mining and metal extraction, further intensification of metallurgical processes with increased metal extraction selectivity and efficiency is needed. Ore grades of available primary ores are decreasing and there is an increasing interest and demand for novel “technology metals”, for example, in renewable energy technologies, such as wind turbines, solar photovoltaic cells, electricity grids and batteries (European Innovation Partnership on Raw Materials, 2018). Such minor metals are often present in low concentrations as accompanying metals (Hagelüken and Meskers, 2010) or contained in complex ores and secondary streams. Finally, research and development efforts towards novel metallurgical processes have been mainly focussing on recycling processes (urban mining), but the recovery of metals from secondary resources such as (mineral) waste materials are becoming more and more important as well (Reuter, 2013). The treatment of such secondary raw materials with challenging physicochemical properties requires the use of innovative technologies to extract metals with respect to natural mineral ores (Reck and Graedel, 2012). Over time, waste management has also evolved from the remediation of large volumes of municipal and industrial waste driven by space, environment and health issues, to the recycling of large volume commodity streams like construction and demolition waste and base metals, such as iron, copper and aluminium. When looking to the case of industrial mineral waste materials (e.g. slags, sludges and ashes), their evolution in waste management starts during the industrial revolution when these wastes were produced for the first time in large quantities. Until the late 1970s, no real waste management legislation was in place for these materials so that uncontrolled landfilling or use as road construction materials took place with the main aim to get rid of these superfluous materials. In several cases, the uncontrolled use of certain waste materials in road construction led to health and environment issues due to the leaching of heavy metals (Vandecasteele et al., 2002). The increasing awareness of the impact of uncontrolled stockpiling and use of mineral waste materials on health and environment in the late 1970s and early 1980s led to increasingly strict legislation on the disposal and use of such materials. This sparked the waste-producing companies to study and implement the remediation of polluted sites and improve the quality of the produced waste materials so that it would be applicable, according to the ruling legislation, as a secondary raw material in several sectors, as

e.g. construction materials. Over the following decades, recycling of waste materials became ever more important in light of preservation and protection of the global environment, but at the same time these resources needed to be economically competitive with primary resources (Reuter et al., 1997; Reuter et al., 2004). Finally in the last two decades, developments towards specificity recycling technologies have emerged, in which technology metals are recovered from selected waste streams according to a product-centric recycling approach (Reuter, 2013). This evolution is driven by the supply needs and cost of specific metals, rendering their recovery economically viable. This implies that stabilisation and solidification of metal-containing mineral waste to fix metals in their matrix and minimise their leaching potential, hence lowering its environmental footprint, is no longer the (sole) strategy. In contrast, the metals (both valuable and hazardous metals) are removed and recovered before applying the mineral residue as an environmentally benign product. Former waste management focused mainly on the end-of-life phase, the phase where ‘material’ became ‘waste’. Managing the material along the whole value chain is essential to find sustainable answers to the waste issue. In this sense, the required systems approach can be considered as a move towards the circular economy. In recent years, research attention is also increasingly drawn to concepts such as *enhanced landfill mining* (ELFM) whereby urban and industrial waste landfills are considered material mines and energy reservoirs (Jones et al., 2013; Quaghebeur et al., 2013).

Thus, over the last decades, the conceptual methodologies of metal mining and production on the one hand and (mineral) waste recycling, on the other hand, have been growing towards each other, as represented in Figure 2. This approach was driven by many technical, social, legislative and economic factors due to increased complexity of the metal mining and production and waste recycling industries and finally requires a cross-over of research challenges regarding metal recovery within mineral waste treatment and primary ore extractive metallurgy within a circular economy approach. There is a need to develop new technologies and processes that will enable the selective and efficient recovery of metals from low-grade material streams to produce a clean mineral residue which can be further valorised. This strategy requires a high degree of flexibility to allow for processing of input materials with variable compositions and properties. In brief, the transformation towards a circular economy and near-zero-waste processing is ongoing, but there are still many challenges hampering its practical implementation.

3. Considerations on ore grades and available low-grade materials

The ore grades and quality have decreased over the decades (Mudd, 2010; Prior et al., 2012; Watling, 2014). The easiest-to-mine

ores have been already exploited, leaving the more complex and less accessible ones. Due to the decreasing grades, more inputs in the form of energy, water, capital and labour are required for the same output and at the same time larger volumes of waste are generated (Prior et al., 2012). Declining ore grades also imply higher refractoriness of the ores and the presence of more impurities (e.g. arsenic or mercury). Despite the decreasing ore grades, global production has continued to grow due to new discoveries, more efficient technologies and higher metal prices (Mudd, 2010). West (2011) has argued that the decrease in metal grades has been driven rather by new technological innovations, which have rendered low-grade ore processing economically viable, than by the depletion of higher-grade resources. In principle, extraction of metals from very low-grade ores (e.g. bedrock) is possible with existing technologies, but the associated costs are still exuberantly high (Steen and Borg, 2002), especially when the grade lays below the so-called “mineralogical barrier” (Skinner, 1979). However, Laznicka (2006) predicted that due to future increasing material demands and consequent increase in metal prices new approaches will be developed enabling recovery of metals from non-conventional resources, such as seawater and ordinary rocks. This highlights the importance of technology development for the processing of difficult-to-process ores and side streams.

Although many non-ferrous metals are recovered in Europe from primary (mining) and secondary resources, their production cannot meet the current demand of the European Union, despite the increasing production from ores and concentrates (Figure 3). The EU has to import some metals despite the relatively large intra-EU production (Supplementary Information).

Therefore, if local low-grade resources could be exploited the self-sufficiency of Europe for metal supply could increase. A detailed description of the origin and properties of the seven example low-grade primary or secondary resources that are present in Europe and discussed in this review paper can be found in the Supplementary Information. These materials were carefully selected because they are generic for Europe and cover a wide range of economically important and critical metals, as well as a wide range of mineralogic compositions. In Europe, these material streams represent a total estimated metal stock worth of over 945 M€ for a total annual production that exceeds 8.5 Mtonne. The base metal concentrations in the low-grade resources discussed in this paper are often close to or in the range of current economic ore grades of primary ores (Table 1).

For the Polish and Greek laterites, the economic value today is almost exclusively determined by their nickel content; the possibility of recovering cobalt may be also considered in the near future. Zinc is

present in both goethite residue and the zinc-rich sludges in similar quantities. Yet, while the economic potential of the zinc-rich sludges is entirely driven by zinc, in goethite residues there are various other high-value metals that raise the overall economic value. However, it might be difficult to valorise the full economic value of goethite when all six considered elements for this material (i.e. Ag, Cu, In, Ni, Pb, Sb and Zn) would need to be recovered. While fayalitic slags and waste chromium-rich neutralisation sludge all have reasonable economic potential, they also stand out in terms of the dispersion of that value across different metal components. Among the listed low-grade primary ores and the secondary industrial residues, zinc is one of the elements whose recovery appears worthwhile. The use of zinc-containing waste sources is restricted due to zinc purity requirements set by the manufacturers and, consequently the recycled to virgin material ratio is critical and only small ratios may be considered for obtaining high purity zinc (Reuter et al., 2002).

In addition, avoided landfill cost is an important parameter of the economic assessment of the management of low-grade secondary mineral waste materials. The higher the landfill costs, the more attractive it is to further process material and try to recover as much as possible of the metal values contained within. The divergence of landfill costs across Europe implies that the economic assessment of the processes could vary considerably based on the location of the operation. On average the cost for landfill is 82.7 EUR per tonne in Europe (CEWEP, 2017).

Apart from the metal content and the landfill costs, several other parameters determine the attractiveness of processing low-grade secondary materials. For example, 40–60% of the total mineral processing costs can be related to mining and crushing (Abramov et al., 2012; Cox et al., 2011; Zhao et al., 2012), which can be avoided as several mineral waste materials are already fine-grained and become available after processing without the need of such activities. The availability of equipment, steam and/or expertise and know-how within the facility producing these streams can also drastically improve the economic potential.

4. Technical aspects

The conventional process flow sheets for metal extraction, whereby ore is transformed into the final product (i.e. metal compound), consists of three main steps:

- (i) The *mineral processing step* (also called *beneficiation step*) whereby the ores are prepared to allow for efficient extraction of metals in the following processing steps. Mineral processing often includes comminution of the ore and concentration of metals in a fraction with an acceptable composition and grade for the next step. Mineral processing thus assures that the metal-containing minerals are sufficiently liberated or accessible for extraction in sufficient grades.
- (ii) The *metal extraction step*, wherein the metals are chemically extracted from their minerals. This process generally consists of one or more pyrometallurgical, hydrometallurgical and/or bio-hydrometallurgical extraction steps.
- (iii) The *metal recovery step*, consisting of refining the mixture of extracted metals to the desired purity and chemical form (i.e. metallic, salt, oxide). In this step the impurities need to be removed.

However, within the zero-waste concept, a fourth important process step needs to be added:

- (iv) the *residue valorisation step*, wherein the residues formed throughout the full metal extraction process are valorised (i.e. transformed into a product). Actually, this step involves more than just the valorisation of the solid matrix material that was originally present in the ore, but also included the closing the loop for

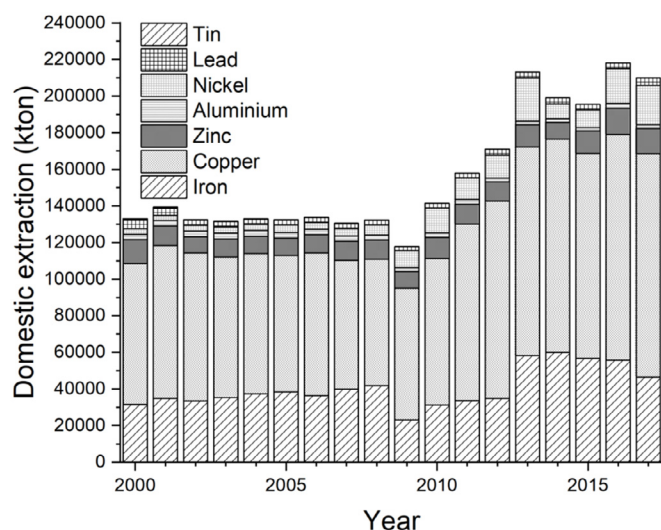


Figure 3. Domestic extraction of base metals in the EU (source: Eurostat)

Table 1

Economic grades, global reserves, production rates and years of supply of some base metals, compared to grades of selected mineral waste streams and low-grade ores.

Metal	Economic ore grade	Reserves	Production	Greek laterite	Polish laterite	Fayalitic slag	Jarosite sludge	Goethite sludge	Chromium-rich neutralisation sludge	Zinc-rich sludge
Unit	%wt	Mtonne of metal	Mtonne/y	%wt	%wt	%wt	%wt	%wt	%wt	%wt
Fe*	30-60	79,000	858	13-32	6.8	42	16.0	24.1	11.4	9.1
Al*	27-29	4675	33	0.39-9.6	0.14	1.6	0.51	0.9	0.13	0.19
Cu*	0.5-2	480	15.3	<dl	0.0001	0.44	0.060	0.4	0.064	0.0007
Pb*	5-10	67	3.4	n.d.	<dl	0.44	2.8	1.8	0.0002	0.0009
Zn*	10-30	220	10	0.009-0.015	0.008	2.4	2.1	5.9	0.0002	5.5
Ni*	1.5-3	64	1.6	0.84-1.00	1.0	0.13	0.0096	n.d.	1.5	0.013
Cr**	20-30	560	30	0.55-1.7	0.041	0.065	0.0086	0.05	2.6	0.006
Co***	0.1-0.4	7	0.123	0.029-0.062	0.16	0.10	0.0001	n.d.	0.031	0.001

* Economic ore grade, Reserves and Production in 2006 as reported by Norgate and Jahanshahi (2010);

** Economic ore grade as reported in (Rötzer and Schmidt, 2018) and Reserves and Production in 2017 as reported in (U.S. Geological Survey, 2018);

*** Economic ore grade as reported by (Cobalt Institute, 2019) and Reserves and Production in 2017 as reported in (U.S. Geological Survey, 2018). Composition of low-grade ores are reported elsewhere: Greek laterite (Miettinen et al., 2019), Polish laterite, fayalitic slag (Yurramendi et al., 2016), jarosite sludge, goethite sludge (Abo Atia and Spooren, 2020), chromium-rich neutralisation sludge (Yurramendi et al., 2016), zinc-rich sludge (Yurramendi et al., 2016).

processing residues, such as wastewaters, waste solvents, exhaust gasses and ashes.

Many efforts have been made by the metal industry to close material loops within their processes and to reduce air and water emissions through application of efficient water treatment and air pollution control systems. However, such systems are not within the scope of this review paper, where we focus on the matrix material valorisation aspect. Figure 4 represents a **new metallurgical systems approach for low-grade resources**, involving a concept beyond a simplistic metal-centric approach, in which only the most valuable metal(s) is (are) extracted and the residual matrix (typically more than 95 wt%) is stockpiled or landfilled. This new approach should allow designing tailored, integrated flow sheets which aim to recover both critical and base metals, while simultaneously lowering the metal content to acceptable levels in order to find sustainable solutions for the valorisation of the residual solid matrix and any other residuals as well. Therefore, a “New Metallurgical Systems toolbox” has been developed within the European METGROW+ project (METGROW+), which consists of a broad range of already existing as well as innovative and under development metallurgical unit operations suitable for low-grade and complex materials, following a value-chain approach, from mineral

processing, to metal extraction, metal recovery and (residual) matrix valorisation. If any remaining residues still need to be disposed of in a waste sink, the risk for metal leakages is diminished.

The overall requirements for the applied unit operation technologies can be summarised as highly selective and efficient metal recovery, low consumption of materials and energy, overall low environmental impact of the process and a final residue which preferably can be used as a novel product or at the most be safely stored without causing environmental hazards. In the following subsections the most salient developments of novel unit process technologies that can serve as future tools to populate the new metallurgical toolbox are discussed.

4.1. Mineral processing

The main goal of all mineral processing operations is to concentrate the minerals of interest and reject the unwanted material associated with the ores/wastes. The process is usually complicated since minerals occur both physically and chemically combined with each other. In general, mineral processing can be divided into three main stages/unit processes: *size reduction* by crushing/grinding, *size control* by screening/classification, *enrichment* by washing/gravity separation/flotation/magnetic separation/preliminary leaching (Gupta and Yan, 2016).

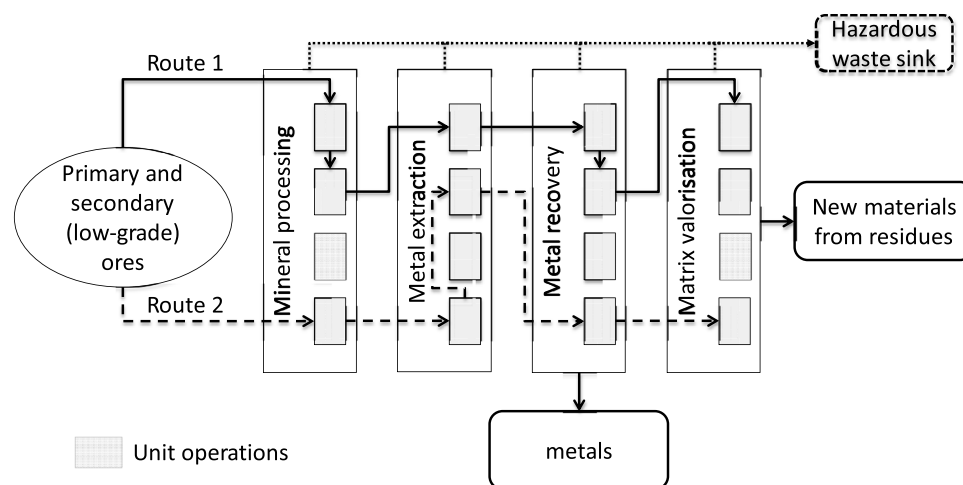


Figure 4. The near-zero-waste new metallurgical systems toolbox proposed by the METGROW+ project (METGROW+). Arrows represent possible process routes connecting different unit operations. The best process routes vary from case to case.

Research related to size reduction focusses particularly on the avoidance of over-grinding and the application of new mineral liberation technologies, such as electrodynamic and microwave fragmentation. Comminution by grinding and milling is an energy-intensive process. The energy required for comminution accounts for roughly 29% of the total energy spent on mining in the USA (DOE, 2007), with 99% energy loss through noise and heat. Over-grinding is very expensive and produces fines that tend to interfere with the subsequent separation process, increasing downstream processing costs (Wang et al., 2012). Microwaves (MW) can penetrate rocks and introduce artificial cracks beneath the surface (Lippiatt and Bourgeois, 2012). The ensuing strength reduction lowers the energy demand for crushing and grinding, by 30% (iron ores) to 70% (mixed sulphides) (Kingman et al., 2004). The cracks are produced around selected mineral boundaries, resulting in higher liberation degrees and ore grade. Electrical fragmentation relies on selective electrical breakdown which allows full liberation without over-grinding (van der Wielen et al., 2013). Electrical comminution was shown to liberate minerals in much coarser fractions with significantly fewer fines than mechanical breakage (Wang et al., 2012).

Beneficiation of ores aims at separating the metal-containing minerals from the gangue material. This poses a particular challenge for low grade primary ores and secondary raw materials as these materials generally are fine-grained in nature or need to be milled to fine particle sizes in order to allow for sufficient mineral liberation. Many conventional physical separation techniques have been found to be inefficient for the treatment of fine particles in terms of selectivity and recovery, mainly due to the low mass, growing influence of fluid drag forces and a high surface area of the treated materials (Figure 5) (Dermont et al., 2008; Fuerstenau and Han, 2003; Gosselin et al., 1999; Svoboda and Fujita, 2003). Inefficiencies in fine particle separation translate into both a large loss of revenue and an unnecessary waste of natural resources. Interesting developments regarding the beneficiation of fine-grained low-grade ores are made in the field of flotation as one of the few technologies that are able to concentrate fine-grained minerals of

interest. Novel “green” flotation agents are being developed based on cellulose to replace the current non-biodegradable and harmful chemicals used (Lopez et al., 2019). Furthermore, to overcome the physical barrier of particle size, whereby ultra-fine particles cannot be separated by froth flotation (Wang et al., 2014), selective flocculation of aggregates of desired minerals to a suitable size for efficient separation during flotation is being developed (Forbes, 2011; Yu et al., 2017).

Other current and future developments in the field of mineral processing are related to digitisation of industrial processes, whereby sensor-based sorting of mineral streams allows the sorting of minerals based on chemical composition and appearance (Robben and Wotruba, 2019) and the eventual implementation of machine learning (McCoy and Auret, 2019) to further improve the processes and allow a higher grade of selectivity and flexibility. The implementation of such technologies will minimise consumption of energy, water and reagents, as well as the amount of generated (mineral) waste.

4.2. Metal extraction

Within zero-waste metal extraction processes of low-grade ores, requirements regarding metal extraction efficiency and selectivity are very demanding. On the one hand, extraction of very low metal concentrations from the matrix material needs to be achieved, to obtain sufficient economic revenue for valuable metals and to lower the concentration of potentially hazardous metals to stringent concentration limits. On the other hand, the metal extraction needs to be achieved with a low impact on the physicochemical properties of the matrix materials, since it requires to be further valorised. Development of novel pyro-, hydro-, bio- and solvometallurgical routes focuses indeed on achieving these goals. In the following sections a selection of promising novel technologies for selective and efficient metal extraction and recovery from low-grade ores, in particular for the materials considered in this work are described.

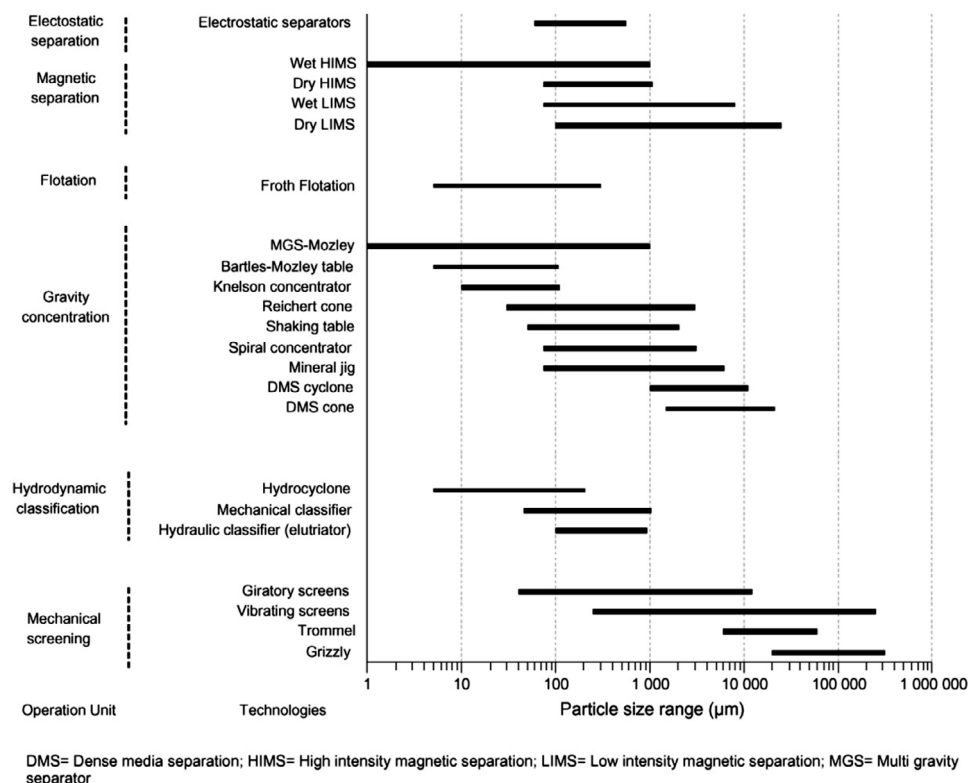


Figure 5. Particle size ranges for physical separation techniques. As reported by Dermont et al., 2008.

4.2.1. Innovation in pyrometallurgical processes

Pyrometallurgical fuming is a technology which focuses on the recovery of metals that can be extracted as fumes (mainly Zn and Pb). In the case of secondary resources, zinc can be recovered by fuming through zinc distillation and/or zinc oxide production with simultaneous reduction of heavy metal impurities in the waste material (Yang et al., 2019). Zinc obtained by such a route can be combined with primary zinc at a high ratio, keeping the impurities below the most demanding requirements (Reuter et al., 2002).

In addition to jarosite and goethite sludges, zinc is also present in fayalitic slags and zinc-rich sludges. The recovery of zinc from these wastes by classical hydrometallurgical processes necessitates large volumes of chemicals with low returns of zinc meaning that they are not economically profitable. Alternatively, several pyrometallurgical processes have been proposed for zinc recovery but few are carried out at industrial scale (Li et al., 2017; Reuter et al., 2002). Problems, such as impact on the environment, low zinc concentration or chloride content in the waste, prevent their industrial implementation.

In order to increase the recovery efficiencies obtained by hydrometallurgical processes, pyrometallurgical techniques have been investigated for several residues such as galvanic sludges (Rossini and Bernardes, 2006), leaching residue from hydrometallurgical production of zinc (Jiang et al., 2017) and electric arc furnace dust (Lin et al., 2017).

4.2.2. Atmospheric and heap leaching

Recovery of metals from primary low-grade and secondary raw materials is often accomplished through leaching with the use of acidic (mainly) or basic solutions. For example, extraction of nickel and cobalt from low-grade laterites (<1.5% Ni) can be carried out through acid leaching and normally involves high acid consumption and the production of large volumes of pregnant leach solutions (PLS) that need to be treated for the removal of impurities and the recovery of valuable metals (Mystrioti et al., 2018). High-pressure acid leaching (HPAL) seems more efficient, in terms of elevated nickel and cobalt and reduced iron, aluminium and magnesium extraction (Georgiou and Papangelakis, 1998; Zhang et al., 2015). However, due to problems related to the harsh conditions prevailing in autoclaves, emphasis during the last years was put on atmospheric leaching (AL) at relatively mild conditions (e.g. 1–5 h residence time, 80–95°C temperature), which is characterised by reduced energy and capital cost (Basturkcü et al., 2017; Kursunoglu and Kaya, 2016; McDonald and Whittington, 2008). During atmospheric leaching, target Ni and Co yield was >90% while acid consumption may be as high as 500 kg/tonne dry ore. Other recent research efforts have concentrated on the use of sulphuric acid to treat low-grade saprolitic nickel laterites with emphasis on mechanisms and kinetics (MacCarthy et al., 2016), sulphuric acid in the presence of sodium sulphide to treat limonitic laterites (Luo et al., 2009) or ferric chloride to treat saprolitic laterites and recover Ni, Co, Mg and Mn (Zhang et al., 2016).

Heap leaching is traditionally used in the mining industry to extract (precious) metals from low-grade ores because of its technical simplicity and low capital cost (Ghorbani et al., 2015; Zambak, 2012). Heap leaching is practised all over the World in three main applications: (i) cyanide leaching of gold ores, (ii) acid leaching of copper oxide ores and (iii) oxidative acid leaching of secondary copper-sulphide ores, invariably with the assistance of certain microorganisms (Petersen, 2016). In heap leaching, excavated low-grade ores are placed in a heap on an impermeable liner and sprinkled with a leach solution for a defined period of time. The pregnant leach solution is collected continuously at the bottom of the heap, with subsequent recovery of the metals. Proper heap operation requires a thorough knowledge of the chemical interactions between the ores and the leaching agent, as well as an optimal design of the heap to avoid permeability problems. In fact, maintaining high heap permeability is the main obstacle to broader implementation of this technology in the mining industry

(Ghorbani et al., 2015).

Heap leaching does have significant potential for low-grade secondary resources, due to its flexibility and low investment costs. In addition, many of the secondary resources of interest are currently placed on well-developed landfills, where much of the required infrastructure (impermeable liners, sprinklers) are already in place. Application of the technology to low-grade secondary resources requires adaptations in leach chemistry, agglomeration and a (near) zero-waste approach for the treated residues (Komnitsas et al., 2019). Sapsford et al., 2016 listed ore processing residues, coal fly and bottom ashes, mining wastes, steel-making dusts, dredging sediments and landfill soil as potential secondary resources to perform *in situ* recovery of metals. Spooren et al., 2016 investigated NaOCl-assisted alkaline heap leaching of chromium and vanadium from slags and found that 11–19% Cr and 7.0–7.5 % V were leached selectively after 64 days. Moreover, the extraction of chromium and vanadium left the matrix material intact, with the potential to even improve the slags' environmental quality. Heap leaching may be also applied for the treatment of low-grade laterite ores, which normally requires longer times and has lower nickel and cobalt recoveries compared to acid leaching in reactors (Agatzini-Leonardou and Zafiratos, 2004; Oxley et al., 2016).

As mentioned earlier, one of the key issues to solve during heap leaching of fine-grained secondary resources is limited permeability. Traditionally, the agglomeration has been performed with a wide variety of binders depending on the leaching chemistry (Ghorbani et al., 2015). These factors will also need to be further investigated in order to improve the efficiency and versatility of the process to account for the low-grade and often alkaline nature of secondary resources.

4.2.3. Bioleaching

Addressing the often high demand of chemicals in conventional leaching processes, alternative, low-impact processes are of increasing interest. Bioleaching is considered a more sustainable method for metal extraction, e.g. the winning of gold, copper, zinc, nickel, cobalt and uranium from their sulphide ores (Brierley and Brierley, 2001; Komnitsas and Pooley, 1989; Schippers et al., 2014). Industrial processes rely on oxidative bioleaching with autotrophic microorganisms, where sulphur and iron-oxidising bacteria (e.g. *Acidithiobacillus*) facilitate the dissolution of metals by either producing powerful leaching agents, such as H₂SO₄ from elemental sulphur, or oxidised metals in sulphidic minerals (Schippers et al., 2014). Therefore, the process requires only the input of O₂ and CO₂ from the atmosphere, as well as some nutrients. Recent studies have proposed widening autotrophic bioleaching method to treating also more challenging secondary resources containing sulphides or elemental sulphur. For example, progress is made in mining tailings and jarosite rejects, earlier considered as waste residues of environmental risk due to residual sulphur species and heavy metals, but contain also valuable metals (Aromaa et al., 2013; Mäkinen et al., 2017). The cost-efficient biological process holds advantages when compared to an energy-intensive pyrometallurgical process, or chemical leaching under harsh conditions. For mine site tailings, Aromaa et al., 2013 showed that bioleaching resulted in higher leaching yield and selectivity for copper, zinc and nickel, compared to chemical leaching. The drawback was lower solid-liquid ratio and longer contact times. Mäkinen et al., 2017 showed that autotrophic microorganisms were able to rapidly convert elemental sulphur of jarosite reject in H₂SO₄ and caused partial dissolution of Zn, Cu and Ge. Other possible mechanisms in autotrophic bioleaching relate to biogenic oxidation of Fe²⁺ to Fe³⁺, which can act as powerful redox-mediator for metallic copper in respective wastes (e.g. electronic scrap, slags from copper refineries), resulting in dissolution of copper with rather mild and inexpensive leaching systems (Mäkinen et al., 2015).

Also, oxidic secondary resources are proposed for treatment by bioleaching methods. For example, *acidithiobacillus ferrooxidans* could reduce Fe³⁺, that was dissolved from limonitic laterite ores, to Fe²⁺ when cultivated under anaerobic conditions and supplemented with

elemental sulphur (Johnson and du Plessis, 2015). Removal of poorly soluble Fe^{3+} increases the dissolution of nickel-bearing iron(III) minerals, such as goethite. Mäkinen et al., 2017 have studied a similar method for treating jarosite where iron is also its trivalent Fe^{3+} form. Jarosite reject contains large concentrations of elemental sulphur, which can be utilised directly and “free-of-charge” in the reductive bioprocess.

Besides the application of acidophilic microorganisms, the use of heterotrophic microorganisms, especially fungi, for bioleaching of non-sulphidic substrates, such as carbonates, silicates and oxides, has also gained attention (Burgstaller and Schinner, 1993). Microorganisms can produce diverse biolixiviants for metal extraction either in immediate contact with the material or indirectly in a separate unit. Heterotrophic bioleaching of low-grade ores has been investigated preliminarily with organic acids, such as oxalic, citric, gluconic, malic and succinic acid, for their proton-donating capacity and ability to intervene in redox reactions and chelation (Burgstaller and Schinner, 1993). The fungal strain *Aspergillus niger*, was investigated for a range of secondary materials such as nickel and zinc leaching from low-grade silicate ores (Castro et al., 2000), leaching of copper and tin in electronic scrap (Brandl et al., 2001), as well as various base metals from fly ash (Wu and Ting, 2006) and Zn refining residues.

In addition to organic acids, large iron chelating biomolecules, e.g. siderophores, produced by heterotrophic microorganisms could provide new routes for selective recovery. Metal chelation moieties, such as hydroxamic acid, catechol, and carboxyl groups (Gadd, 2010) have a high affinity for iron cations, while also binding and solubilising other metals effectively (Bau et al., 2013). Relatively unexplored biolixiviants include biosurfactants, such as rhamnolipids, which have been principally applied for soil remediation (Chen et al., 2017). Biosurfactants are produced by a large variety of microorganisms (bacteria, yeast and filamentous fungi) with different molecular structures (Sarubbo et al., 2015). In general, surfactants are amphoteric molecules consisting of a nonpolar tail and a polar head. In aqueous solutions, surfactants reduce surface tension by accumulating at the solid interfaces and facilitating desorption of metals from the material (Miller, 1995). In addition, biosurfactants can be composed out of polysaccharides, peptides and lipids having various functional groups (carboxylic, phosphate, sulphate groups) that provide metal chelating properties.

Yet, cost-effective mass production of biolixiviants with heterotrophic microorganisms can be a challenge. Various studies have shown proof of using cheap and renewable substrates or organic waste streams. For example, the use of molasses, potato peels, sawdust, corn kernel, corn husk for culturing of *Aspergillus niger* for the production of a variety of organic acids was reported by Mulligan and Kamali (2003).

4.2.4. Solvometallurgical leaching

Solvometallurgy is a relatively new branch of extractive metallurgy that can complement pyrometallurgy and hydrometallurgy. Solvometallurgy beholds the extraction of metals from ores, tailings, industrial process residues, production scrap and urban waste using non-aqueous solutions (Binnemans and Jones, 2017). Most of the unit processes in solvometallurgy are very similar to those in hydrometallurgy, with the main difference being that water is replaced by a non-aqueous solvent. For instance, in hydrometallurgy, leaching is performed with aqueous solutions of acids or bases, or chelating agents, whereas in solvometallurgy leaching is done with acid-saturated neutral or basic extractants, acidic extractants, chelating extractants diluted in non-polar organic solvents; acid-saturated polar solvents; halogens in organic solvents. Some solvometallurgical processes make use of solvent-water mixtures, but the solvent concentration is assumed to be at least 50 vol%.

Solvometallurgy can offer several advantages compared to conventional hydrometallurgical processes. One obvious advantage is the reduced consumption of water and the generation of smaller volumes of wastewater. By direct solid leaching or non-aqueous slurry solvent

leaching, the processes of leaching and solvent extraction can be combined into a single step, leading to process intensification. Hydrometallurgical processes with acid leaching are not very compatible with carbonate-rich ores and especially not with those rich in calcite or dolomite, because the dissolution of the carbonate gangue material consumes large amounts of acids. This is relevant if the minerals in a carbonate matrix cannot be separated from the gangue by flotation. By solvent leaching the ore minerals, the carbonate gangue materials can be left largely untouched. Because solvent leaching is more selective than leaching with aqueous solutions of mineral acids, it is possible to avoid the co-dissolution of unwanted metals such as iron, which also leads to a reduction in the consumption of acids. Solvent leaching can, in principle, offer a higher selectivity than leaching with aqueous solutions of acids (H_2SO_4 , HNO_3 , HCl), especially if chelating extractants are used, such as the LIX family of extractants. The use of solvents also makes it easier to leach silicate ores, because in conventional leaching with acids there are often serious issues with silica gel formation.

The concept of solvometallurgy originates from research activities in the United States shortly after World War II, aimed at recovering uranium from domestic uranium ores (Bailes and Magner, 1957). These were typically low-grade uranium ores with a U_3O_8 content of less than 1%, such as low-lime sandstone ores containing carnotite, autunite, torbernite and uranophane or high-lime carnotite ores containing high concentrations of calcite (CaCO_3) gangue material. Three different solvometallurgical processes for uranium recovery from low-grade ores have been disclosed.

Solvometallurgy also proved to be useful for the recovery of copper from chrysocolla ($\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$). The recovery of copper from chrysocolla by direct acid leaching is challenging because of the formation of silica gel. Raghavan and Fuerstenau developed a solvometallurgical process for the recovery of copper from chrysocolla by leaching it with the extractant LIX 63 dissolved in kerosene, in the presence of a small amount of aqueous ammonia solution (Raghavan and Fuerstenau, 1993; Raghavan et al., 1979; Raghavan et al., 1981).

A solvometallurgical process has been developed for the recovery of zinc from different chloride-containing solid residues: zinc ash from galvanising baths, and flue dusts from the zinc smelting and Waelz processes (Thorsen et al., 1981). The solvometallurgical process is based on the reaction of the fine-grained ZnO with acidic extractants, and in particular with carboxylic acids such as naphthenic acids and Versatic acid.

During the past two decades, Russian researchers have developed several processes for the recovery of valuable metals from refractory ores and ores rich in soluble silica (e.g. eudialyte) that are difficult to treat using conventional hydrometallurgical processes (Chekmarev et al., 2001; Chizhevskaya et al., 1994). A common feature of these solvometallurgical processes is the combination of mechanical activation with solvent leaching. It was found that the leaching efficiency was considerably improved with this mechanical activation step. Kopkova has found that a titanomagnetite concentrate could be decomposed by an organic solvent consisting of *n*-octanol saturated with concentrated HCl (Kopkova et al., 2015).

4.2.5. Extraction using Deep Eutectic Solvents

Ionic liquids (ILs) have gained attention due to their attractive properties, such as non-flammability, chemical stability, high thermal stability and low volatility (Zainal-Abidin et al., 2017). Despite their advantages, ILs generate concerns about their application due to their toxicity and the high costs associated with their synthesis and purification. Thus, the search for alternative solvents led to the study of deep eutectic solvents (DES) for the extraction of valuable compounds. DES show similar physicochemical characteristics to those of ILs but higher biodegradability, lower toxicity and lower synthesis costs (Kareem et al., 2010; Tang et al., 2015; van Osch et al., 2015). These characteristics have propitiated their use as extractants for metals

recovery (Abbott et al., 2004).

DES has been introduced by Abbott et al., 2004 as mixtures consisting of a hydrogen-bonding acceptor and a hydrogen-bonding donor (Li et al., 2016). Due to their eutectic nature, the melting points of DES are significantly lower than the melting points of their components (Zainal-Abidin et al., 2017). Abbott et al. (Abbott et al., 2004; Abbott et al., 2006; Jenkin et al., 2016) have tested DES as extractant agents for the recovery of several metals. According to the results, the metals can be extracted by the DES if they are in their oxidised form. The high efficiency of the extraction of metals of interest such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn by means of the application of DES composed by choline chloride and malonic acid has been demonstrated (Abbott et al., 2006). Interesting results have also been obtained with DES formed by choline chloride and other carboxylic acids, such as oxalic acid (Abbott et al., 2004), and for the extraction of gold, silver and rare earths using choline chloride:ethylene glycol DES (Jenkin et al., 2016). Although DES based on carboxylic acids can dissolve many metal oxides, a recent study has to be shown that there can be issues with esterification reactions between the alcohol group of choline cation and the carboxyl group of the carboxylic acid (Rodrigues et al., 2019). A new DES consisting of *p*-toluenesulfonic acid monohydrate:choline chloride is a good solvent for metal oxides (Rodriguez et al., 2019).

A key aspect to minimise the process wastes and reach the (near) zero-waste approach is the reuse/recycling of the DES after the metal extraction and recovery. However, this topic has not been widely studied up to now due to the novelty of the use of DES as extractants. The use of a “one-pot” strategy with the combination of metals extraction using DES and electrowinning techniques (see Section 4.3.4) for the recovery of the metals would allow the recovery and recycling of the DES during several operation cycles. The degradation of DES during the operation must be assessed to determine the maximum number of cycles and the need to partially replace the extractant with fresh DES.

4.3. Metal recovery

The development of efficient processes for the recovery of metals after the extraction step is key for the successful integration of low-grade ores and secondary sources as inputs in the new metallurgical schemes. The heterogeneity in the composition and the presence of impurities often found in these streams, as well as the low concentration of the desired metals, will imply a challenge in the concentration of the metal(s) of interest in a solution or substrate with uniform characteristics. Thus, the development of flexible and, at the same time, highly selective processes is required. On the other hand, the common issues linked to metal recovery processes are the toxicity and cost of extractants, toxic emissions and, particularly important, the wastes generated in the recovery processes, as the intention is the prevention of waste generation by recycling or reusing the extractants, diluents or products used after the metals have been concentrated.

Increasing interest arises on novel ionometallurgical, electrochemical and biotechnological approaches for metals recovery. Such technologies, which will be further described below and show interesting advantages in relation to conventional metal extraction options. General reasons for the use of these iono-, electro- and bio-approaches are (i) process intensification (different unit operations can be combined, e.g. extraction using ionic solvents and electrodeposition), (ii) higher selectivity (e.g. through voltage tuning in electrodeposition, the choice of the ionic solvent or of the bioabsorbent), (iii) reduced energy consumption due to the possibility to work at room temperature and (iv) reduction of harmful emissions.

4.3.1. Solvent extraction

The down-stream processes used for the purification of *pregnant leach solutions* (PLS), obtained either from atmospheric, pressure or heap leaching of ores such as laterites, aim at the recovery of valuable elements including Ni, Co and in some cases Mg, and the separation of

impurities including Fe, Al, Zn, Cu, Cr and Mn. These processes, which normally involve the steps of precipitation, solvent extraction and electrowinning may differ depending on the quality of PLS, the concentration of each element and the desirable form of the recovered metal of interest (Agatzini-Leonardou et al., 2009; Gao et al., 2014; Mihaylov et al., 2000; Moskalyk and Alfantazi, 2002). More recent research efforts attempt to increase efficiency and improve the economics of these processes. Cheng et al., 2010 reported that the separation of Ni and Co from impurities such as Mn, Mg and Ca using solvent extraction with Versatic Acid 10 was largely improved by the addition of a synergistic reagent LIX63 (an α -hydroxyoxime) or 4PC (a pyridine carboxylate ester). Cheng et al., 2015 used a synergistic solvent extraction (SSX) system, consisting of Versatic Acid 10 and Acorga CLX 50 in ShellSol 2046, to recover Ni and Co from laterite leach solutions and separate them from Mn, Ca and Mg, which proved more cost-effective compared to the traditional precipitation and re-leaching method. Over 99% of Ni and Co was extracted using four stages of semi-continuous extraction while more than 80% of the Mn was rejected to the raffinate. The co-extraction of Ca was less than 5% while the co-extraction of Mg was negligible. Liu and Lee (2015) investigated the separation of Ni and Co from chloride leaching solutions with solvent extraction using D2EHPA and LIX63 in a pH range 1–3; the extraction percentages of Ni and Co were 62% and 96% respectively. Since no commercial process exists today for the recovery of Ni and Co from a nitrate-based laterite leach liquor, Hutton-Ashkenny et al., 2015 investigated the efficiency of solvent extraction, which is a commercially proven extraction process for Ni and Co from sulphate-based laterite leach liquors, at the Direct Nickel pilot plant in Australia. Three different solvent extraction systems, involving neodecanoic acid (Versatic™ Acid 10)/tributylphosphate (TBP), Versatic Acid 10/pyridine carboxylate (PC), and an aliphatic hydroxyoxime based extractant (LIX 63)/Versatic Acid 10/PC were tested to separate Ni and Co from Mg and Mn. Their results indicated that the synergistic combination of Versatic Acid 10 and a pyridine carboxylate (in this case nonyl-4-PC) was identified as the most promising system. Meng et al., 2015 investigated the purification of PLS obtained after hydrochloric acid leaching of Ni laterite and serpentine ores and the production of Ni–Co precipitates, MnO₂, and MgO. The recoveries of Ni, Co, Mn, and Mg were nearly 100%, 93%, 94%, and 99%, respectively. Zhu et al., 2017 used the ionic liquid extractant trihexyltetradecylphosphonium chloride (Cyphos IL 101) to study the recovery of Co and Mn from synthetic nickel laterite leach solutions containing chloride. It was shown that Co and Mn were effectively extracted from a solution containing 100 g/L Cl with 0.5M Cyphos IL 101 in the pH range of 1.2–4.5, whereas no significant Ni, Mg and Ca were extracted.

4.3.2. Supporting Liquid Membranes (SLM) using ionic solvents

Liquid membrane processes have been suggested as a clean technology due to their characteristics of high specificity, a minimal amount of solvent needed, high intensity and productivity as well as low emissions and low energy requirements. Moreover, the extraction and stripping steps typical of the other separation technologies, such as liquid-liquid extraction, are reduced to a single step in liquid membranes (De Agreda et al., 2011; Lozano et al., 2011). The applications of membrane contactors are of interest for metal recovery in water and integrated process solution. It has been found to be a cost-effective technology used to supplant or replace other technologies, membrane-based or not (Pabby and Sastre, 2013). The membranes are wetted with the specific extractants. Different membrane configurations are shown in Figure 6 and Figure 7. Recently, the use of ionic liquids as extractants in liquid membranes is being studied, due to its benefits in comparison with common extractants. The use of ionic liquids in this application results in membrane stabilisation due to their negligible vapour pressure, possibility of minimising their solubility in the surrounding phases and greater capillary force associated with their high viscosity (Malik et al., 2011). For example, Zante et al., 2019 successfully separated

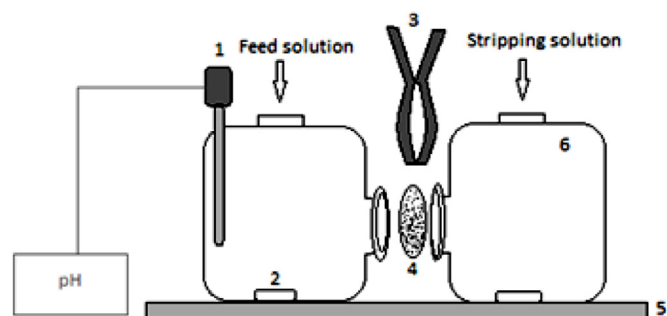


Figure 6. Example of flat-sheet supported liquid membrane configuration (1) pH meter, (2) stirring bar (3) clamp (4) flat sheet membrane (5) magnetic stirrer (6) cell

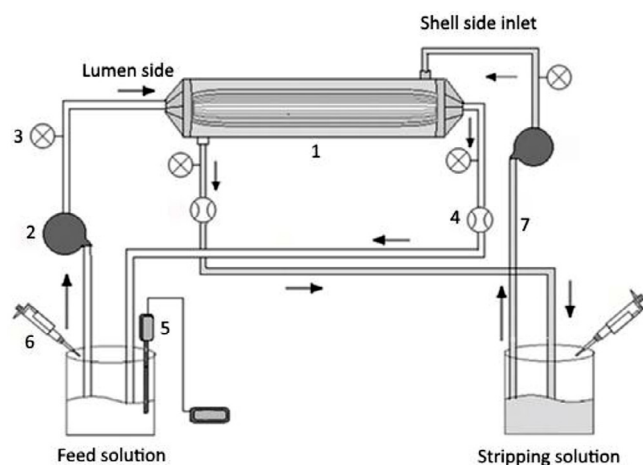


Figure 7. Schematic counter-current – flow diagram in a hollow fibre supported liquid membrane, (1) membrane contactor, (2) gear pump, (3) pressure gauge, (4) flow meter, (5) pH meter, (6) pipette for taking samples, (7) pump tubing

lithium from cobalt, nickel and magnesium ions in acidic aqueous solutions by using supported ionic liquid membranes with tributyl phosphate as extractant (Zante et al., 2019). Also, Jean et al., 2018 used supported liquid membranes with the ionic liquid iso-octylmethylimidazolium bis-2-ethylhexylphosphate as a carrier for heavy metal ions extraction, finding that the system was more suitable for soft cations (Hg(II), Cd(II)) than hard cations. However, no studies about the use of deep eutectic solvents as extractants in liquid membranes have been found, which could be a potential field of study. It should be realised that for this application new hydrophobic DES must be developed, because all conventional are totally miscible with water.

4.3.3. Supported ionic liquid phases (SILPs)

The recovery of metal ions from dilute aqueous streams with ion-exchange resins or chelating resins suffers often from the slow diffusion of metal ions in the solid resin particles. A novel approach is the use of *supported ionic liquid phases* (SILPs) for the recovery of the valuable metals from diluted aqueous waste streams. In SILPs, an ionic liquid phase is immobilised on a high-surface-area solid support by impregnation or by covalent attaching of the ionic liquid cation (Riisager et al., 2006). The SILP concept was developed for catalysis, but it proves to be useful in the field of metal recovery as well. The SILPs combine the advantages of ionic liquid solvent extraction systems and ion-exchange resins and are very useful for the recovery of metals from diluted aqueous streams. First of all, a much smaller volume of ionic liquid is required for a SILP than for a bulk ionic liquid extraction phase, because the ionic liquid is coated as a thin film on a solid support. Secondly, the strong interactions between the ionic liquid molecules and

the solid inorganic support can largely reduce losses of the ionic liquid by leaking into the aqueous phase. Thirdly, the ionic liquid can act as an extractant itself by an anion exchange mechanism or the ionic liquid can serve as a diluent for the extractant. SILPs are a very versatile technology and can be applied to different aqueous waste streams and leachates.

Recently, a SILP process has been developed to selectively recover indium from iron-rich leachates (Van Roosendaal et al., 2019). The SILP used in this study was synthesised by impregnating Amberlite XAD-16N with the iodide form of the quaternary ammonium ionic liquid Aliquat 336. Adsorption was preceded by the addition of an excess of iodide anions to the solution, to form indium iodide species, which were extracted to the ionic liquid of the SILP. High selectivity for indium over iron could be achieved because iron iodide species are not stable in aqueous solutions. The developed indium recovery process was validated on real leachate of goethite residue. A pure indium solution of 49 mg L^{-1} was obtained with an indium-over-iron mass ratio of 7.9 and a selectivity factor equal to 5400. A similar process was developed for the recovery of germanium from iron-rich aqueous solutions with a SILP comprising the ionic liquid Aliquat 336 impregnated on Amberlite XAD-16N (Van Roosendaal et al., 2019). Adsorption was preceded by the addition of citrate anions to the iron-rich aqueous solutions, to form germanium(IV) citrate complexes, which were extracted to the ionic liquid layer of the SILP. A germanium solution of 44 mg L^{-1} was obtained from a goethite leach solution, with a germanium-over-iron mass ratio of 39. This corresponds to a selectivity factor equal to 34400.

4.3.4. Metal electrodeposition from Deep Eutectic Solvents

Electrodeposition is a process leading to the formation of solid materials by electrochemical reactions in a liquid phase (Zhang et al., 2012). The setup is composed of a three-electrode electrochemical cell where the metal contained in the electrolyte is reduced at the cathode and deposited in metallic form (Figure 8).

Generally, metal electrodeposition is carried out through an acid or basic aqueous solution. This process needs high temperatures for achieving suitable efficiencies and, furthermore, aqueous baths are known for their toxicity. The use of DES, that can also be used for metal extraction as discussed before, are promising substitutes to these

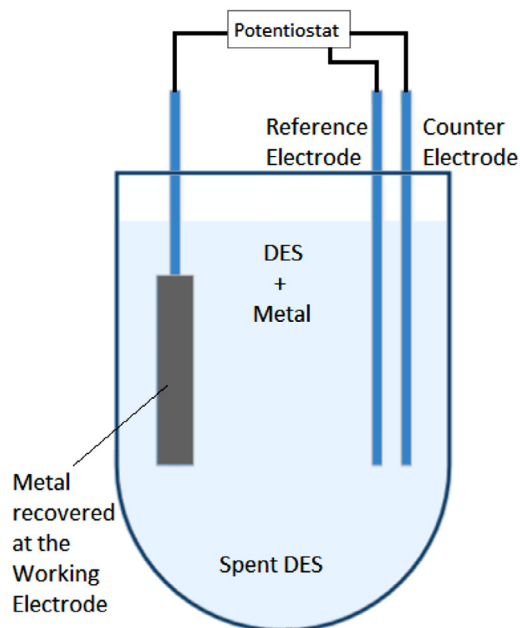


Figure 8. Representation of a three-electrode electrochemical cell for metal electrodeposition from DES

aqueous solutions. DES are well suited for metal deposit as they are cheap, easy to prepare, easily biodegradable and not harmful for the environment compared to most of the other ionic liquids (Mares Badea et al., 2014). Many favourable properties such as good thermal stability, high metal solubility and moisture stability enhance the interest in deep eutectic solvents (Abbott et al., 2003; Zhang et al., 2012). With low water content, DES present a wider potential window reducing the effects of hydrogen evolution and allowing the electrodeposition of some elements such as light and refractory metals. The temperature of operation can be kept under 90°C or even at room temperature, with still favourable results.

4.3.5. Bioprecipitation

Bioprecipitation by *sulphate reducing bacteria* (SRB) is commercially utilised for remediation of acidic mine drainage and wastewater from various metallurgical processes (Sánchez-Andrea et al., 2014). Dissimilatory sulphate reduction is found in a variety of microbes, both in bacteria (*Deltaproteobacteria*, *Nitrospirae*, *Clostridia*, *Thermodesulphobiaceae*, *Thermodesulphobacteria*) and *Archaea* (Muyzer and Stams, 2008). In general, the sulphate reducing bacteria prefer an environment with a pH between 6 and 8 (Widdel, 1988). However, both acidophilic and alkaliphilic SRB have been isolated. Bioprecipitation through SRB has potential in the recovery of metals locked in secondary solid materials, such as low-grade ores, metallurgical slags and industrial sludges, following the leaching with sulphuric acid or through bioleaching. Furthermore, sulphate is a common impurity in waters from hydrometallurgical processing, since metals are mostly recovered from ore bodies containing sulphidic minerals, which oxidise to sulphate during metal extraction (Lopez et al., 2009). Following-on, the sulphate in the subsequent leachate is reduced to biogenic sulphide by the activity of SRB. Metal sulphide precipitation obeys fixed formation constants, allowing for selective recovery with usually low solubility and hence low residual metal concentrations (Gadd and White, 1993; Hao et al., 1996; Neculita et al., 2007). Tuning the pH largely contributes to the selective recovery of metals and hence a higher purity in the obtained solids (Tabak et al., 2003). Metal sulphide precipitates have a low moisture and high metal content that is beneficial for further refining at a smelter and explains their reasonable market value.

Clearly, most of the commercial SRB applications have focused on sulphate (and metal) containing wastewater treatment. However, H₂S can also be biologically produced from elemental sulphur, resulting in similar metal sulphides of high purity. Paques installed the largest biological H₂S generator in the World at the Pueblo Viejo gold mine in Dominican Republic to produce approximately 20 tonne per day of H₂S gas from elemental sulphur to recover copper. The bioreactor is fully operated at ambient temperature and pressure. In the process that is set up as in multi-stages, sulphate is reduced to sulphide in a separate bioreactor. Since the SRB is in that case never in direct contact with the process solution, they can thus handle streams of various composition and avoid inhibiting effects due to toxicity (Sánchez-Andrea et al., 2016). It is the first biological on-site and on-demand production of biogenic sulphide using sulphate reducing bacteria (SRB) (Isosaari and Sillanpää, 2017). Hydrogen sulphide gas is transported to a second metal precipitation stage where the precipitation reaction takes place and purified water is retained (Sánchez-Andrea et al., 2014). Single-stage processes, where sulphate reduction and metal precipitation occur in the same reactor (Kaksonen et al., 2003), certainly have a lower investment cost, yet operating expenditures should also be a part of the decision when choosing between a single or multi-stage process (Gopi Kiran et al., 2017).

Hao et al., 2016 suggest that SRB based systems anyhow can recover from certain temperature fluctuations, which is important when operating continuously and the waste water temperature varies due to e.g. meteorological conditions.

4.3.6. Biosorption

Biosorption has been used as an all-encompassing umbrella term for the removal and remediation of soluble metals and metalloids by biologically sourced materials. Usually, biosorption refers to the passive uptake of elements by deactivated and pre-treated biological materials (Volesky and Holan, 1995). The active bio-mineralisation of metals by living microorganisms, especially bacteria, avails as it can renew substrates without the addition of external materials. It has been investigated from scientific perspectives to principally understand their fundamental role in the geochemical cycling of metals in the biosphere (Gadd, 1999) and for the engineered remediation of metals from aqueous matrices (Gadd, 2010). Phenomena using viable cells attributed to dissimilative anaerobic respiration, e.g. U(VI) reduction to less mobile and less toxic U(III) by archetypal dissimilative bacteria of the *Shewanella* and *Geobacter* genus (Lovley, 1993). Activity of *Pseudomonas* strains may furthermore reduce the toxicity of soluble Ag⁺ species through an electrochemical reduction to zero-valent Ag nanoparticles (Klaus et al., 1999). Other immobilization mechanisms extend to active surface groups that possess a high affinity for metals or through active cellular uptake in micelles, resulting in a bio-composite. Metal recovery using such approach further shifts the paradigm from remediation and recovery of metals to green synthesis of e.g. bio-nanoparticles (Hennebel et al., 2009).

4.4. Residue valorisation

4.4.1. Residue valorisation as construction materials: opportunities

Massive amounts of construction materials are required to satisfy the infrastructure and housing needs of the growing global economy. Due to its low cost and versatility concrete is by far the most popular construction material, making it second only to water as the commodity most used by mankind. At a scale of production of 30 Gt/y (Barcelo et al., 2013), the extraction of resources to make concrete products has a major impact on the environment. Concrete is composed of on average 85% of aggregates and 15% of binder. This implies that a very significant share of the 40 Gt/y extracted construction aggregates is used in concrete applications (UEPG, 2016). More than 99% of concrete uses Portland cement as a binder. The current production of Portland cement consumes an estimated 5 Gt/y of raw materials, primarily limestone and clays. The production process involves the calcination of the limestone and subsequent conversion to the Portland cement clinker at 1450°C. The CO₂ released by cement production thus contributes to about 8–10% of global anthropogenic CO₂ emissions (Scrivener et al., 2016). In response, the cement and concrete industries have increased their efforts to develop and implement the use of secondary raw materials and low-CO₂ binders (Van Deventer et al., 2012). This drive towards diversification of resources and binders is creating leverage and opportunities for upcycling of residues into construction materials.

4.4.2. Upcycling of residues in cements and binders

There are several approaches towards upcycling of inorganic residues as a binder for concrete products. First is as a substitute raw material for the production of Portland clinker. The level of substitution depends on the chemical composition of the residues and is usually low, i.e. a few percent, for residues poor in CaO. A second route is the replacement of Portland clinker by a residue-derived *supplementary cementitious material* (SCM). Finally, a third route is to use residues as the major constituent of an alternative binder. In this respect *alkali-activated materials* (AAMs) – also known as *inorganic polymers* – have been widely investigated. The main opportunities and challenges of SCM and AAM technologies for upcycling of residues are discussed below.

4.4.2.1. Supplementary cementitious materials. SCMs are used in combination with Portland cement and contribute to the performance of hardened concrete by means of a chemical reaction. This chemical reaction is usually of hydraulic or pozzolanic nature. Hydraulic

materials set and harden spontaneously when mixed with water. Pozzolanic materials require water and calcium hydroxide to react and harden (Snellings et al., 2012). Calcium hydroxide is a product of Portland cement hydration. Hydraulic materials can replace up to 95% of the Portland clinker while pozzolanic materials are limited to 55% replacement. Iron blast furnace slags and coal combustion fly ashes are widely used and regulated as hydraulic and pozzolanic SCMs, respectively. A conservative estimate of their global use is 650 Mtonne/y (Snellings, 2016).

In contrast, slags and sludges from non-ferrous extractive metallurgy have not been adopted as SCM for cements so far. The effect of adding slags from the copper, lead and zinc production as SCM on the strength development has been widely studied on lab-scale, with results ranging from a performance comparable to an inert filler up to pozzolanic activities similar to or exceeding coal fly ash (Benkendorff, 2013; Edwin et al., 2016; Hallet et al., 2019; Sanchez de Rojas et al., 2008). This spread on reactivity can be explained next to fineness by variations in chemistry (e.g. CaO content) (Simon et al., 2018) and differences in phase composition such as amorphous phase content, due to different cooling methods (Pontikes et al., 2013; Siakati et al., 2019). The performance of sludges, such as bauxite residue (Pera et al., 1997; Ribeiro et al., 2011) or jarosite (Arora et al., 2015; Gupta and Prasad, 2018), is also dependent on their chemistry and pretreatment processes (CaO addition or calcination) which influences the reactivity and phase assemblage after hydration. In general, the main technical challenges to resolve are: (i) the content and emissions of contaminants, (ii) compounds incompatible with Portland cement, generating long-term instabilities of the concrete end-products and (iii) low reactivity and little contribution to the performance of the concrete. Key to overcoming these barriers is the development of pre-treatment processes that extract potentially valuable contaminants, neutralise or remove incompatible compounds and deliver reactive materials fit for use. In view of these aspects, metal extraction and recovery (described above) are crucial, not only from the perspective of recovering valuable metals, but also from the perspective of delivering clean and reactive SCMs.

4.4.2.2. Alkali-activated materials. Alkali-activated materials are formed by mixing two components, a solid silicate precursor and an alkaline activating solution (Komnitsas and Zaharaki, 2007; Provis et al., 2015). After the dissolution of the precursor, a binder precipitates or polymerises and the resulting paste sets and hardens, usually at room temperature. The solid precursors can be metallurgical residues but the materials most often used are fly ash from coal combustion, metakaolin, as well as ground granulated blast furnace slag from iron production (Provis et al., 2015). These materials can be used alone or in binary/ternary mixtures. With respect to the alkaline activators, these are usually concentrated solutions of (sodium, potassium) hydroxides and (sodium, potassium) silicates. In the literature, the term “geopolymer” is often used for denoting the alkali-activated material, although strictly the term is reserved for the product of aluminosilicates (metakaolin, coal fly ash) mixed with alkali-silicate solutions (Davidovits, 1989).

Like SCMs, the potential emission of contaminants from non-ferrous slags and sludges can be a problem. This similarity to SCMs does not extrapolate to the problem of low reactivity. The higher alkalinity of the system causes several non-ferrous slags to have a significant reactivity and strength development. Slags from secondary copper production and the gasification of landfill mining residues have successfully been incorporated as 100% of the precursor of alkali-activated materials in lab and pilot-scale experiments (Denissen et al., 2019; Iacobescu et al., 2017; Machiels et al., 2017). Similarly, lead slags (Onisei et al., 2012), ferronickel slags (Komnitsas et al., 2019; Komnitsas et al., 2006; Maragkos et al., 2009) and fayalitic slags (Komnitsas et al., 2020) have shown promising mechanical performance at lab-scale. The successful use of sludges is less reported, although research into the use of for instance bauxite residue is ongoing. This can for instance be applied in alkali-activated materials when adding a pyrometallurgical treatment

(Hertel et al., 2016; Hu et al., 2019).

In general, new binders such as inorganic polymers or new SCMs, which have been subjected to detailed investigation only recently, cannot rely on decades of in-service testing and durability data to prove their long-term stability. Therefore, the first step to widespread application is the use of new binders in low risk, non-structural concrete products. Simultaneously the development of performance-based standards is required to regulate their use for more demanding products (Van Deventer et al., 2012).

5. Economic, sustainability, environmental and safety impact

From a sustainability perspective, new processes and flowsheets must be both economically viable and beneficial for the environment and society as a whole. Therefore, an integrated approach covering the techno-economic analysis, an environmental impact assessment as well as a hazard and risk assessment are required. Only when a rigorous assessment is performed during the design and operational stages of a process, the optimal route can be identified. Such assessment can include process modelling via tools (such as HSC Sim or METSIM) and engineering design in combination with different of assessment methods such as economic (LCC), environmental (LCA), exergy analysis that allows determination of flows in terms of quantity and quality, losses and emissions in a more rigorous way (Abadías Llamas et al., 2019; Abadías Llamas et al., 2019; Castro et al., 2007; Ignatenko et al., 2007), statistical entropy analysis for quantifying the potential of a system to concentrate or dilute substances (Rechberger and Brunner, 2002; Velázquez Martínez et al., 2019) and safety evaluation. When these analyses are performed early on, a good understanding of the impact that technology and research breakthroughs may have on the financial viability and sustainability of a metallurgical system can be obtained (Buyle et al., 2019; Hoogmartens et al., 2014; Thomassen et al., 2016). In this way, it is ensured that research will not only focus on profit maximisation, but also on achieving medium and long term environmental credits.

From the sustainability assessments carried out in various research projects (Thomassen et al., 2016; Van Dael et al., 2014) it can be concluded that technology developers for metal recovery of low-grade primary and secondary resources should strive for efficient processes where energy, water and chemicals are recovered and re-used as much as possible. In case the use of auxiliary materials is substantial, it is worth looking for the development of a less expensive and/or more environmentally friendly alternatives. Attractive valorisation routes for the depleted matrix material remaining after treatment of low-grade resources and other by-products is not only crucial for targeting a near-zero-waste approach, but also for the economic and environmental performance of the whole flowsheet. Although revenues are mainly dependent on the sale of the extracted metals and the direct value of by-products is mostly inferior, the latter gains are important because of the prevention of landfilling for large volumes of residues in the form of solids or slurries and the reduction of associated landfill expenses. For secondary mineral materials, the avoidance of landfill costs is also a crucial aspect that drives the business case. Although a large variety exists across EU countries, the cost for landfilling a waste material is considerable. In case an industrial facility can prevent landfilling and generate business instead this certainly will result in a more attractive financial picture.

Environmental impacts from new developed technologies for metal recovery from low-grade resources are compensated by the avoidance of impacts from conventional metal production (Nuss and Eckelman, 2014), the avoidance of landfilling of remaining waste and the valorisation of the metal-depleted matrix and other by-products as e.g. construction materials such as aggregates or supplementary cementitious materials. Because the produced tonnage of these by-products is much higher than the tonnage of the produced target metals, the valorisation of second-grade resources is crucial in calculating the

overall avoided impact of the considered processes. The positive impacts from avoiding landfilling strongly depend on the type of waste material to be landfilled. For instance, landfilling of inert waste is associated with relatively low climate-change impacts, whereas landfilling as refinery sludge is associated with high impacts for several LCA impact categories, such as, climate change, 'eutrophication potential, smog generation potential, ecotoxicity and human toxicity. Hence, the avoidance of landfilling an inert waste will not, as such, drive the environmental attractiveness of the process. Assessment of technologies used for the treatment of low-grade resources generally indicate lower impacts for several LCA-categories when no waste remains after the process. Moreover, recently, it was also observed that predicted net profits were significantly negatively correlated with environmental impacts (e.g. ecotoxicity, acidification, eutrophication, ozone depletion), implicating that processes resulting in lower environmental impacts are expected to result in larger profits (Nys et al., 2020).

Apart from landfill costs, numerical variation in various other location-bound parameters, such as, labour costs, transport distances, electricity cost and energy mix, is expansive among European countries, and have a major influence in the financial outcome and the environmental attractiveness of a process.

Finally, a proper health and safety hazard assessment of the by-products based on their complete chemical and mineralogical composition as well as the toxicity of their constituents is crucial in order to determine their accurate hazard profile and identify potential barriers for their use, such as a predicted classification of process residues as 'substances of high concern' due to the presence of remaining hazardous metal fractions, e.g. hexavalent chromium and other hazardous elements (Komnitsas et al., 2019; Mambote et al., 2001).

6. The need for new business models

A circular economy approach ensures that materials are retained within productive use, in a high-value state, for as long as possible (Antikainen and Valkokari, 2016; Ellen MacArthur Foundation, 2015; Ritzén and Sandström, 2017). It focuses on reshaping business and economic systems so that waste is 'designed out'. In a circular economy, not only pollution is reduced, but the systems are designed to repair the previous damage (Murray et al., 2017). Innovating the business model (i.e. updating the elements of an existing business model or establishing a new organisation and associated business model) to embed, implement and capitalise on circular economy practices is seen as a solution. Evolving from a traditional to a circular business model, not only impacts the internal activities, but also extends the link between supply chain members. While the concept of "circular business models" covers various aspects, leasing of products is a more prominent part of it.

Furthermore, integrating a (near)-zero-waste approach in practice requires an adaptation of existing economic business models to render the approach economically viable. In this respect, the budding literature on *Enhanced Landfill Mining* (ELFM) and urban mining has addressed some of the primary issues that need to be considered while evaluating the economic potential of low-grade (secondary) resource processing. While from an environmental perspective the primary focus will often be on the recovery of materials, the economic costs of the operational processes generally outweigh the revenues from the extracted commodities (Krook and Baas, 2013; Krook et al., 2012; Van Passel et al., 2013). In this light, Danthurebandara et al., 2015 conclude that the economic performance of ELFM rests not only on relevant technologies, but also on markets (e.g. electricity price) and on regulations determining the price of green certificates and the fraction of green energy. Additionally, each landfill and urban mine has specific characteristics that need to be analysed prior to proceeding with excavation.

A general characteristic of any business model in the near-zero-waste context will include the valorisation of each generated stream. For instance, the calorific content of Refuse Derived Fuel in landfill

mining projects contributes substantially to the determination of the net present value of a project (Danthurebandara et al., 2015). Moreover, the excavation process can also create clear possibilities for synergies by integrating a relevant ELFM project with infrastructure or real estate projects (Van Passel et al., 2013). Hence, a successful business model requires businesses to move beyond their core expertise and create strategic alliances. The incomplete value chains can hinder the circular economy transformation for certain secondary materials, but subsequently, unconventional business opportunities are provided for new stakeholders (Kinnunen and Kaksonen, 2019). Krook and Baas (2013) argue that cross-sectoral cooperation between entities could ensure that the costs and benefits related to the excavation of materials are shared among the different parties involved. This cooperation will create a more complex value chain but could also allow projects that would otherwise not be viable, to proceed profitably. Currently, government intervention through the provision of green certificates nevertheless remains essential in ensuring that economic benefits outweigh costs (Van Passel et al., 2013). Increasing commodity costs and potential future supply shortages could supply a boost to Urban Mining and ELFM projects in the future (Schulte, 2013), as well as the processing of low-grade ores. However, the recovered materials compete on the same output market as those originating from exploited (high-grade) natural sources (Krook and Baas, 2013). While in the long run the expected price evolution could make the excavation of landfills and urban mines economically interesting, the sensitivity of a project to any potential short-term price fluctuations in those same markets require careful *ex-ante* consideration by the business. Hence, it is important that each process in the process is subjected to thorough sensitivity analyses to obtain indications of both the upside and downside risks faced.

In addition, the integration of metal refining and recycling can widen companies' participation in the value chain. One example of such integration is Boliden, which operates in primary metals extraction and recycling (Florin et al., 2015). As a result of integration, materials sourcing and business models get more stable and also the investment costs can be at least partly avoided.

A zero-waste approach thus needs to move beyond the exclusive focus on the recovery of deposited resources. Moreover, through co-operation businesses need to be involved in long-term learning processes to obtain the required know-how (Krook and Baas, 2013).

7. Conclusions

With low-grade primary ores starting to be cost-effectively mined and many metals becoming critical, the industry in Europe and elsewhere is at the verge of mining a myriad of low-grade primary and secondary mineral materials. Examples of such low-grade European resources include Greek and Polish laterites, fayalitic slags, jarosite, goethite and chromium-rich and zinc-rich landfilled sludges, which contain industrial and economical relevant base and critical metals. Conventional metal recovery technologies developed for high-grade ores do not suffice for these complex low-grade materials, for which tailored solutions are needed. Research continues to develop novel technologies and complete flow-sheets to extract and recover metals more selectively by improving mineral processing and pyro-, hydro-, solvo- and biometallurgical processes. Technologies described in this review represent novel opportunities for metals recovery from low-grade materials. Most of the described technologies have been tested only in laboratory environments so far and need further development prior to actual industrial applications. The main challenges related to pre-treatment are fine particle sizes of secondary material streams and how to avoid over-grinding. Some novel technologies in metal extraction and recovery, such as solvents and DES, require rather expensive chemicals, and recycling of these reagents is crucial in getting the technologies to the use in industry. In biohydrometallurgy, the tolerance of microorganisms is of concern and needs special attention, when designing process flow sheets. In waste valorisation, not all materials

can be used as such in construction applications, but for example mixing of two materials can enhance needed properties. Therefore, these technologies need further development and their suitability must be always considered case-by-case.

Metal recovery from low-grade ores can only be viable when near-zero-waste routes are implemented and also the metal depleted residues can be valorised and used in several sectors. Therefore, from a technical point of view, the applied processing technologies are required to be more efficient and innocuous to health and environment. The remaining mineral residue after metal extraction needs to be clean to enable the use as a secondary raw material for novel products, such as construction materials. This adds the benefit of avoiding loss of materials in landfills and ponds. Thus, in this work, the use of a new metallurgical systems toolbox is proposed. Such toolbox should allow treating diverse and complex low-grade metal resources through a flexible combination of unit operations that can be divided into four categories: (i) mineral processing, (ii) metal extraction, (iii) metal recovery and (iv) matrix valorisation techniques. This concept goes beyond a simplistic metal-centric approach as both metals and matrix materials are valorised in the most efficient manner according to a near-zero-waste principle. Therefore, from the economical point of view, such processes need to be fitted into new (circular) business models, whereby costs and profits are divided over the value chain.

Author Contributions

J.S. ideated, edited and proofread the full manuscript and organized the contributions by all co-authors. Following co-authors have particularly assisted in proofreading: K.Bi., K.K., L.H. and P.K. The following sections have been drafted by the respective co-authors: 1. J.S.; 2. J.S.; 3. J.S., G.P., W.K.; 4.1. J.S.; 4.2.1. L.Y.; 4.2.2. G.P., J.S., L.H., K.K.; 4.2.3. K.F., J.V., J.M.; 4.2.4. K.Bi.; 4.2.5. M.G.-M.; 4.3.1. K.Bi.; 4.3.2-4. M.G.-M., M.L., M.T., K.Bi.; 4.3.5. J.B., K.W.; 4.3.6. J.V., K.F., J.M.; 4.4. A.P., R.S., S.O., Y.P.; 5. K.Br., K.O., Y.D.; 6. K.Br., Y.D., P.K.; 7. J.S. P.K.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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